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A B S T R A C T

An improved, pollution free iron and steel pickling and pickle liquor regeneration process is described in which discharge of acid solution and other pollutants from the process circuit is entirely avoided. Pickling is conducted in an aqueous sulphuric acid bath which is indirectly heated and actively agitated to increase pickling efficiency. Some water is removed from the bath through evaporation. Spent pickle liquor is treated in an iron removal operation in which it is cooled to precipitate dissolved iron as ferrous sulphate heptahydrate. This precipitate is separated from the solution and the iron-depleted solution is recycled to the pickling bath. Pickled material removed from the pickling bath is rinsed in two stages with fresh water being added in the second or final rinsing stage at a rate which is controlled such that water input to the rinse is equal to that required to maintain the water balance in the pickling operation. Used rinse water from the final rinsing stage is passed to the first rinsing stage and used rinse water from the first stage is passed to the pickling bath at the rate required to maintain the water balance therein.

This invention relates to an improved process for pickling iron and steel and, more particularly, to an improved process for efficiently pickling iron and steel and effectively rinsing the pickled material in which the entire system is a closed-loop system requiring no waste water treatment facilities and yielding only ferrous sulphate heptahydrate for disposal.

In the steel industry, the steel products obtained by hot milling usually have a tarnished surface due to rust and scale formed thereon. Commonly, the products are treated by a pickling process to remove the rust and scale so as to obtain the desired bright finish to the final products or to enable subsequent working of the semi-finished products.

In carrying out the pickling process, the steel products requiring treatment are immersed in a pickling bath consisting of aqueous sulphuric acid solution, either on a continuous or batch basis, so that the rust and scale are dissolved in the acid solution to form soluble ferrous sulphate. After the material is free of rust and scale, it is removed from the bath and is rinsed with a liberal amount of fresh water to remove acid residual adhering to the surface of the material.

During the pickling operation, acid is consumed in the formation of soluble iron sulphates and the acid concentration in the pickle liquor decreases as the dissolved iron concentration increases. Hence, the acid strength continuously drops in the pickling operation and the time required to pickle the steel increases. Fresh acid can be added to maintain the acid concentration at optimum levels, but eventually the dissolved iron concentration reaches a saturation level and it is necessary to dump the solution from the pickling tank and replace it with fresh solution.

The pickling rate may be accelerated by heating the pickling bath to an optimum temperature. This is usually done by injecting live steam thereinto. This results in the release of a highly corrosive fog or mist from the pickling bath and also condensation of the large amount of steam used in the normal course of the pickling operation increases the volume of the pickling solution, thereby diluting the acid concentration and causing the pickling tanks to overflow unless provision is made for orderly disposal of excess solution.

10 Pickling steel in sulphuric acid solution in the above described manner thus produces these separate waste products: (1) spent pickle liquor, including the extra volume resulting from dilution where heating is done by steam injection; (2) rinse water; and (3) acid droplets in the exhaust from the heated pickle bath.

The disposal of these waste products presents a very serious problem to the primary and secondary steel industries, particularly with the advent of increasingly stringent anti-pollution laws.

20 An improved process for pickling iron and steel is described in United States patent No. 3,575,711 issued on April 20, 1971 to the present inventor, in which a combination of pickling and pickle liquor regeneration is used. The process involves conducting the pickling operation in an aqueous sulphuric acid bath heated by indirect means, such as heating coils, to a temperature of about 140°F. to 180°F. Air is diffused into the bath to actively agitate it. The indirect heating eliminates the introduction of excess water into the pickling bath while the air agitation ensures uniform conditions of temperature and solution composition throughout the bath, thus increasing the overall pickling rate. When the dissolved iron content has built up to between about 8 and about 12% by weight, solution from the bath

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is then passed to an iron removal operation in which the solution is cooled to precipitate the dissolved iron as ferrous sulphate heptahydrate. The solution from the iron removal step is re-used in another pickling operation, while the pickled material removed from the pickling bath is washed with water to rinse off the acid adhering on the surfaces of the pickled material. A part of the rinse water is recycled to the pickling bath to replace the acid and water removed from the system with the ferrous sulphate heptahydrate and a part is discharged from the process circuit, usually after neutralization with lime. While this process avoids many of the pollution problems normally associated with acid pickling operations, it is not entirely satisfactory in this respect. The prior process envisages the removal of a substantial part of the excess rinse solution from the system in non-polluting form by controlling the degree of air agitation to effect evaporation of the excess. However, due to the heat requirements for large scale evaporation, it is generally economic and practical to remove only a relatively small amount of the excess rinse water from the system through evaporation. As a result, a relatively large quantity of dilute acid rinse water is discharged from the system and disposal of this solution presents a serious problem.

According to the present invention, discharge of rinse water from the process circuit of the above noted patent is economically and effectively eliminated altogether by conducting the rinsing operation such that the total water input into the rinsing circuit is such that all the water used in the rinsing operation can be passed to the pickling bath to maintain the water balance of the overall process circuit. That is, the bath is heated and agitated as required to promote efficient pickling and evaporation inherently occurs but the amount of water loss

through evaporation is not necessarily increased as a means of eliminating excess water as is the case with the process of the prior patent. More specifically, the rinsing operation of the invention is conducted in two stages with the freshly pickled material being rinsed first in a primary rinse to remove the major portion of the residual acid on the surfaces thereof. The material from this primary rinse is then rinsed with fresh water in a secondary rinse in which the rate of fresh water addition is no greater than that required to add the amount of water needed to maintain the water balance in the pickling bath. All rinse water from the secondary rinse is passed to the primary rinse and rinse water from the primary rinse is passed to the pickling bath at the rate required to maintain the water balance therein. A surprising feature of this rinsing procedure is that very efficient rinsing can be achieved with the input of a relatively small amount of fresh water. In fact, it is satisfactory if rinsing can be obtained with addition of about one-tenth the amount of fresh water used in previous practice provided rinsing is conducted in two or more stages as just described with the fresh water being applied as the last stage. The ability to achieve a complete rinse with a small input of fresh water in turn permits utilization of all the used rinse water for maintenance of the water balance in the pickle bath without the need for evaporating large amounts of excess water thereby eliminating any waste water discharge from the process. The rate of water addition necessary to maintain the water balance in the pickling bath in any specific case will depend on a number of factors. In most cases, water will be removed from the pickling bath on a continuing basis through evaporation and on either a batch or continuing basis through removal of spent pickle liquor to the iron removal operation. Water is added with recycled, regenerated pickle liquor from the iron removal operation and with the added acid and wash water. The difference between the water added from these sources and the water removed is made up by addition of used rinse water to the system as required.

The process is described in more detail hereinbelow by reference to the drawing which is a schematic representation of an exemplary embodiment of the invention.

In the embodiment illustrated in the drawing, the process may be carried out on either a continuous or batch basis. For simplicity, the process on a batch basis is first presented. The pickling operation is carried out in a pickle tank 10 containing an aqueous sulphuric acid pickling solution. The pickling solution is indirectly heated by steam S circulated through a heat exchanger 11 as shown by the arrows in the drawing. The pickling solution is maintained at a temperature in the range of about 140°F. to 180°F. and preferably between 158°F. to 160°F. to obtain an optimum pickling rate and to prevent crystallization of iron salts in the pickling tank.

The pickling solution is actively agitated preferably by air bubbles produced by air fed through line 13 by air pump 12 to spargers 15 located at the bottom of the tank. The active agitation effectively ensures uniform conditions of temperature and solution composition throughout the bath, thereby ensuring a maximum pickling rate and productive capacity for any given installation.

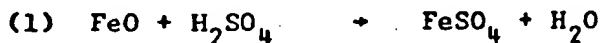
Due to the elevated temperature of the pickling solution, acid and water are constantly evaporating from the pickling solution. The vapours are diverted by a push/pull air curtain to an acid mist filter 16. The air curtain is effected by extruding an air stream over the pickling bath, which may also be conveniently supplied by air pump 12. The mist filter collects the vapours through duct 17, releases the water vapour to the atmosphere and returns the acid condensation continuously back to the tank via line 19 for re-use. The mist or vapour collection is further enhanced by the provision of an exhaust fan 20.

The pickling operation is carried out with an aqueous acid solution containing about 8% to 20% and preferably about 15% to 20% by weight of sulphuric acid. The acid concentration of the pickling solution is maintained within this optimum range by the addition of concentrated acid, when required, to compensate for the acid consumed in the bath for the formation of ferrous sulphate. Inhibitor compound may be added in the solution in amounts as deemed necessary for prevailing conditions as in common practice.

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Improved pickling is obtainable with a dual acid pickling solution which includes an addition of 1% to 3% by weight of hydrochloric acid in the sulphuric acid bath. By the addition of hydrochloric acid in the pickling bath, some of the rust and scale of the pickling article reacts with the hydrochloric acid to form ferrous chloride and water. The ferrous chloride thus formed further reacts with the sulphuric acid to form ferrous sulphate and hydrochloric acid. These chemical reactions are shown in the following chemical equations:

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As can be seen from equations (2) and (3) the reactions are reversible regarding the liberation of HCl. Therefore, the system produces a single by-product namely, ferrous sulphate (FeSO_4) regardless of whether sulphuric acid is used singly or with the addition of hydrochloric acid for pickling. The consumable acid is the sulphuric acid, and in either case, the amount of sulphuric acid used is essentially the same since in the dual acid solution essentially all of the hydrochloric acid is regenerated in the reversible chemical reaction.

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After removal of scale and rust in the pickling operation, the pickled products are removed from the pickling bath and transferred to a primary dunk rinse tank 21 which contains a batch of still rinse water 22. Preferably, the amount of still rinse water 22 is at least equal to the amount of water that will be depleted from a batch of spent pickle liquor by the formation of ferrous sulphate heptahydrate crystals. About 70% to 80% of the acid on the surface of the pickled material is removed in the primary rinse. After treatment in the primary rinse, the material

10 is passed to a secondary or final rinse operation 25 in which the article is rinsed with a fine spray of fresh water supplied to spray headers 26 through inlet conduit 27. The final rinse may be conducted in part as a dunk rinse but it is essential that the fresh water added in the rinse be sprayed onto the material as the final step of the rinsing operation. The amount of fresh water used for the final rinse is about equal to the amount of water required to maintain the water balance in the pickling bath. The rate of addition of water will depend, of course, on the rate of withdrawal of used rinse solution from the rinsing circuit.

20 This rate of withdrawal will depend, in turn, on the water requirements of the pickling operation at any given point of time. When the pickling operation is conducted on a batch basis, the only water loss during the course of pickling operation will be through evaporation. Thus, during such operation, the rate of fresh water addition (and used rinse water removal will be about the same as the rate of water removal through evaporation. The evaporation rate from the pickle batch can be controlled to a certain degree by control of the heat input by heat exchanger 11 and the degree of agitation of the bath, all in line with main-

30 taining the bath temperature within the desired range as previously noted. In general, it has been found that satisfactory rinsing

can be obtained with a fresh water input rate equivalent to the water evaporation rate resulting when the bath is operated with the minimum heat input needed for efficient pickling. That is, it is not necessary to add heat beyond that required for efficient pickling merely for the purpose of increasing the rate of evaporation and thereby to enable an increase in the rate of fresh water addition.

Rinse water from the final or secondary rinse operation 25 is passed to the primary rinse tank 21 by means of transfer pump 28. Rinse solution from the primary rinse bath 22 is
10 passed to the pickling tank 10 by means of transfer pump 29. Normally, the acidity of the primary rinse water will gradually increase to about $\frac{1}{10}$ th of the bath strength as more and more pickled material is washed therein; however, this increasing acidity does not affect the ability of the primary rinse to remove 80% to 90% of the residual acid from the pickled articles.

The pickling process is continued until the ferrous sulphate concentration in the liquor reaches the level equivalent to about 8% to about 12% by weight of dissolved iron and then
20 the entire batch of pickle liquor in the pickling tank 10 is transferred by pickle liquor pump 30 via conduit 31 to the crystallizer 34 for iron removal.

In the crystallizer 34, the pickle liquor is cooled by natural evaporation and by a cooling coil supplied with chilled water from a closed-loop refrigeration system 37. Chilled water is circulated through the coil through inlet conduit 38 and outlet conduit 39.

As the pickle liquor is cooled in the crystallizer 34, ferrous sulphate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) crystallizes out when
30 the solution is cooled to below 90°F. and preferably to about 50°F. When the crystallization process of the dissolved ferrous

sulphate has ceased, the crystals are passed from the crystallizer 34 to a vacuum de-watering box 36 where the crystals are separated from the solution and washed with fresh water supplied through conduit 37 to sprays 38. All of the iron depleted solution may be passed to the de-watering box with the crystals or a part may be passed directly to storage tank 41 via by-pass line 46. The wash water for the crystals together with any separated iron-depleted solution is passed to storage tank 41 via drain line 42. The air discharge from vacuum pump 43 passes through a separator 44 to effect removal of entrained acid and the acid is passed to storage tank 41 via conduit 45. Fresh acid from a supply tank 47 is added to the iron-depleted solution to adjust the acidity to the level required for a fresh batch of pickling solution of the next pickling process.

The ferrous sulphate heptahydrate crystals are released through outlet B of the de-watering box 32 for use or disposal.

The iron-depleted solution in tank 41 preferably is maintained at an elevated temperature of about 140°F. by a heat exchanger 48 which may be heated by the same steam supply as heat exchanger 11 in the pickling bath.

When a new batch of pickling liquor is required, the iron-depleted solution in storage tank 41 is transferred back to the pickling tank 10 by acid transfer pump 49 and, at the same time, a batch of rinse water from the primary rinse tank 21 is also transferred to the pickling tank 10 by pump 29 to make up the water removed from the system with the ferrous sulphate heptahydrate crystals. Alternatively, primary rinse water may be transferred to the storage tank 41 so that a complete batch of fresh pickling solution is always available for transfer to the pickling tank 10 when it is required. It will be appreciated that in either case, transfer of rinse solution from the primary rinse tank 21 to make up a fresh batch of pickling solution will leave room for an

increased fresh water input into the rinse circuit. This can be done on a batch basis, i.e. simply by adding fresh water to the primary rinse tank or, alternatively, the amount of fresh water supplied to the secondary rinse through inlet 27 can be increased until the solution in the primary rinse tank 21 is built up to the desired level.

10 The water used to wash the ferrous sulphate heptahydrate in the de-watering box 36 is fed into storage tank 41 along with the iron depleted solution in order to help replace the water loss through crystallization in the overall process. In any case, the amount of water from this crystal washing operation is negligible compared to the amount of water cycled from the primary rinse bath 21. Therefore, it is essentially the cycling of the primary rinse water into the pickling bath that serves to maintain the water balance in the system for the overall process.

20 The pickling operation may also be conducted on a continuous basis by operating the pickling bath at an 8% to 12% iron content level and continuously bleeding sufficient solution from the bath to maintain the iron at such level while continuously adding sufficient acid to maintain the acid level and sufficient regenerated pickle liquor and primary rinse water to maintain the water level. In such case, rinse water from the primary rinse is cycled to the pickling operation at a sufficient rate to compensate for water losses occurring both from evaporation and removal of ferrous sulphate heptahydrate from the system.

30 It is apparent from the above description that the process of the present invention yields only ferrous sulphate heptahydrate crystals for outside disposal, all the acid besides that consumed in the formation of ferrous sulphate is recycled in the system, and all the used rinse water is employed for maintaining the water balance in the system. Therefore, the present

process is essentially a closed-loop system requiring no waste water treatment facilities.

It will be understood that modifications may be made in the improved process of this invention without departing from the scope of the appended claims.

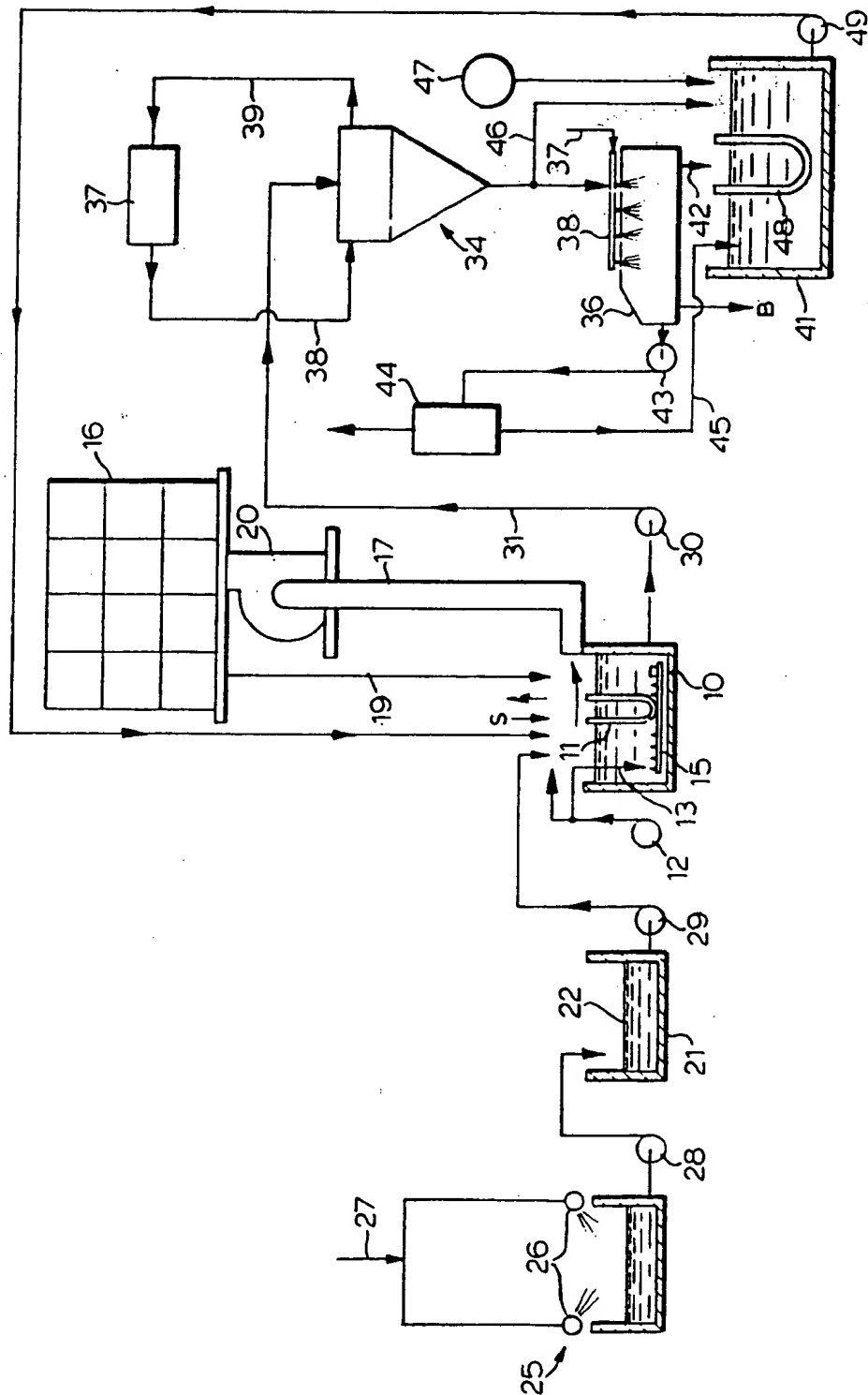
The embodiments of the invention in which an exclusive property or privilege is claimed, are defined as follows:

1. In the process for pickling of iron and steel in a pickling bath containing an aqueous sulphuric acid solution which is indirectly heated and is actively agitated to increase the pickling rate, some water in said pickling bath is removed through evaporation, pickled material is removed from the bath and rinsed to remove the residual pickle liquor therefrom, spent solution from the pickling bath is passed to an iron removal operation in which the solution is cooled to precipitate the dissolved iron as ferrous sulphate heptahydrate, and the iron-depleted solution is re-used in another pickling operation; the improved method in combination therewith for operating the process as a closed-loop system in which no waste acid solution is discharged therefrom, which comprises: rinsing the pickled material removed from the pickling bath in a primary rinse to remove the major portion of the residual acid on the surface thereof; rinsing material from said primary rinse in a secondary rinse with fresh water supplied at a rate no greater than that required to add the amount of water needed to maintain the water balance in the pickling operation; passing all of the rinse water from said secondary rinse to said primary rinse and passing rinse water from said primary rinse to said pickling bath at the rate required to maintain the water balance therein.

2. The process according to claim 1 wherein the pickling is conducted on a batch basis with spent solution being passed to the iron removal operation on a batch basis and being replaced with fresh solution on a batch basis and wherein during the continuance of a pickling operation, fresh water is supplied to the secondary rinsing operation at about the same rate that water is removed from the pickling bath through evaporation.

3. A process according to claim 1 in which an amount of hydrochloric acid in the range of 1% to 3% by weight is added into the aqueous sulphuric acid solution.





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